

IMPROVING GERMANIUM DETECTOR RESOLUTION AND RELIABILITY

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ABSTRACT

High purity germanium (HPGe) detectors used in radionuclide assay systems such as Radionuclide Aerosol Sampler/Analyzer (RASA) systems must operate unattended for long periods of time. Currently, the performance and reliability of commercially available large (~100%) HPGe detectors are acceptable for the majority of laboratory applications. However, for remote systems designed for nuclear detonation detection and analysis, improved performance and reliability are required. The goals of this research include improving germanium detector reliability and resolution performance by developing new surface passivation techniques coupled with a unique detector contact arrangement. A major reliability improvement would be realized if germanium detectors were made less sensitive to storage and operational environments by improving the film coating used to passivate and protect the intercontact surface. This research is the investigation of two surface film techniques for passivating HPGe detector surfaces. Wet chemically grown oxide films and sputtered film coatings will in turn be applied to two standard P-type HPGe coaxial detectors. Each coating will be characterized to determine their surface chemistry passivating qualities as well as their inherent noise contribution to the overall system noise. The resolution of a germanium detector is a function of electrical noise and the inherent resolution of the detector element.

The electrical noise components which reduce the signal to noise ratio of a detector system are associated with detector leakage current, intercontact surface noise, contact noise and noise sources associated with preamplifier electronics. In particular, those noise components associated with the intercontact surface are leakage current and surface noise. We believe these two significant sources of noise can be reduced by using novel surface passivation techniques resulting in improved detector resolution. The techniques developed by this research will be applicable to new detectors and can also be applied as a retrofit to existing RASA units. This will improve the ability to obtain more sensitive and reliable detections of remote nuclear activity.

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OBJECTIVES

State of the art large-volume germanium photon detectors comprise a volume of high purity germanium, an n^+ hole blocking contact (lithium diffusion), a p^+ electron blocking contact (boron implant) and an intercontact surface. The performance of an HPGe detector depends on the electrical characteristics of each of its constituent components. The base material must be "detector grade" HPGe, meaning that it must have a sufficiently low concentration of electrically active impurities (net concentration of $\sim 10^{10} \text{ cm}^{-3}$), have acceptable crystallography, and contain no appreciable concentration of deep levels usually associated with trapping and charge recombination centers. The electrical contacts which create the diode structure, and collect charge created by photon interactions, must be non-injecting and sufficiently robust to tolerate handling in a usual semiconductor manufacturing environment. Furthermore, the contacts must be completely tolerant of all stresses imposed as the detector is held in its vacuum cryostat. An intercontact surface is necessary for electrical separation of the detector contacts. It must allow very little reverse leakage current under the stress of as much as 5000 V of reverse bias. In addition the intercontact surface must create little electrical noise. Both surface leakage noise and passivant dielectric noise must not significantly deteriorate the system signal to noise ratio.

CANBERRA manufactures large HPGe coaxial detectors fabricated from both P-type HPGe and N-type HPGe. For the purpose of this research a CANBERRA version of the P-type coaxial detector configuration will be used. Our primary P-type coaxial detector product is the Standard Electrode Germanium (SEGe), which comprises a right circular cylinder with an outer wrap-around lithium n^+ contact and a boron implanted p^+ center or core contact. The intercontact surface is limited to a small annular region near the core by a unique wrap-around lithium contact. The ruggedness and stability of the contacts have been proven by their use on thousands of standard and special products provided by CANBERRA. Therefore, we will concentrate our reliability and performance improvement efforts on the intercontact surface. The geometry and contact configuration of the SEGe product is schematically represented by Figure 1.

Typically, HPGe detectors can develop poor resolution due to charge carrier injection current caused by contact imperfections or damage as well as surface leakage current caused by intercontact surface channels or carrier generation sites. The surface of single crystal germanium oxidizes readily when exposed to oxygen or water vapor, so it must be chemically passivated to prevent the uncontrolled growth of native oxide. Uncontrolled oxidation of germanium by exposing the surface to atmospheric oxygen and water vapor or to very fast oxidation from acid etches yields porous, low-density oxide films containing non-stoichiometric GeO_x species. A poorly formed native oxide on the intercontact surface of a HPGe detector is unacceptable because such a native oxide layer often contains a significant density of electronic states. Native oxide layers containing empty states with energy levels in the germanium band gap can be positively charged which in turn accumulate electrons to the germanium surface region creating an inversion layer in P-type material or an accumulation layer in N-type material. Such effects in P-type germanium have been described by Brown (1953). Slow states in the oxide layer and fast states in the oxide/germanium interfacial layer have been investigated by Bardeen et al. (1956). Because electrons are attracted to the surface, band bending leads to the formation of weak field regions. More pronounced band bending inevitably creates conductive surface channels. The surface channel model was expanded to describe detector dead-layer effects by Dinger (1975). Hull and Pehl (1994) demonstrated how the temperature sensitivity of surface channels in HPGe can deteriorate detector performance. Furthermore, in the case of P-type material, inversion layers may lead to 1/f noise as reported by MacRae (1960).

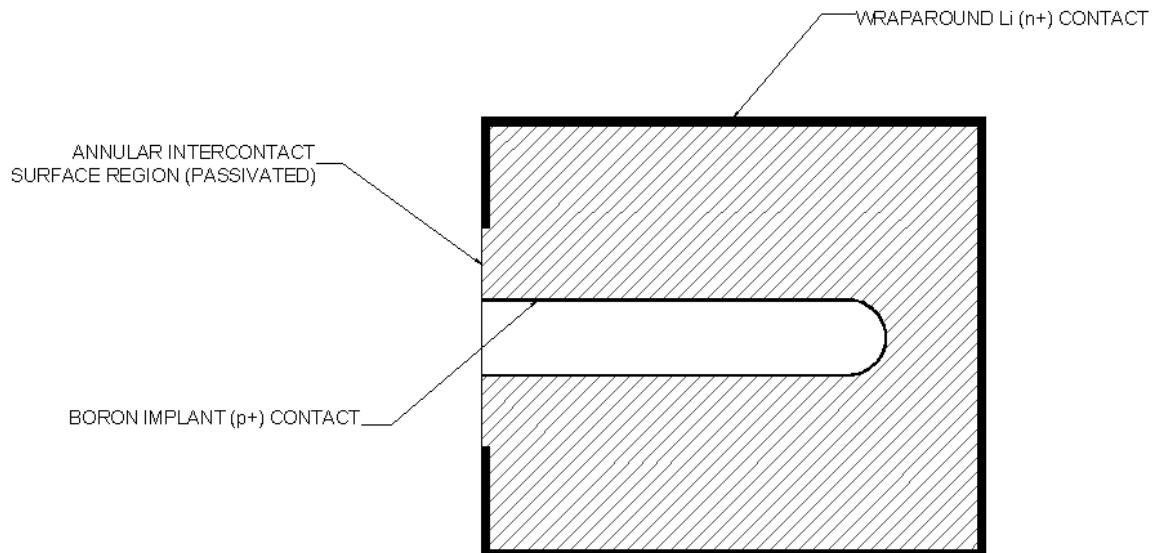


Figure 1. Schematic representation of the CANBERRA SEGe detector element.

As mentioned previously, it is imperative to chemically stabilize the intercontact surface of a germanium detector by passivation. Passivation in the world of HPGe detectors means to coat the intercontact surface using a high resistivity, low-loss dielectric containing a negligible density of electronic states. At CANBERRA, the intercontact surface of our SEGe detector is coated with a layer of SiO_x where x is approximately 2. This coating is created by a well controlled evaporation of silicon monoxide, the methodology being a textbook subject described in many works such as the one by L. Holland (1970). The intercontact region is manufactured by first mechanically polishing the surface to remove gross damage left from the machining process. Microscopic damage is removed by a concentrated nitric acid based etch followed by water and methanol rinses. Subsequently, the intercontact surface is coated with a SiO_x film approximately 100 nm thick using a silicon monoxide evaporation technique.

Although SiO_x passivations have been an acceptable solution for our commercial detector products, some variability in reverse leakage currents as well as field-line distortion effects associated with intercontact surfaces have been observed. Some of the properties of evaporated silicon monoxide on germanium which result in deleterious surface effects have been investigated by Dinger (1976). The existence of weak-field regions and surface channels result from both fast electronic states (germanium surface) and slow electronic states (SiO_x film, adsorbed gases). The charging of electronic states results in band-bending near the intercontact surface as well as field-line termination at the intercontact surface. The band-bending effect of an inversion layer created by positively charged oxide and surface states is represented by the energy-band diagram in Figure 2. Although these effects have been somewhat curtailed by the application of our unique wrap-around lithium n^+ contact, a more consistently neutral intercontact surface may be possible by improving or replacing the present SiO_x passivation.

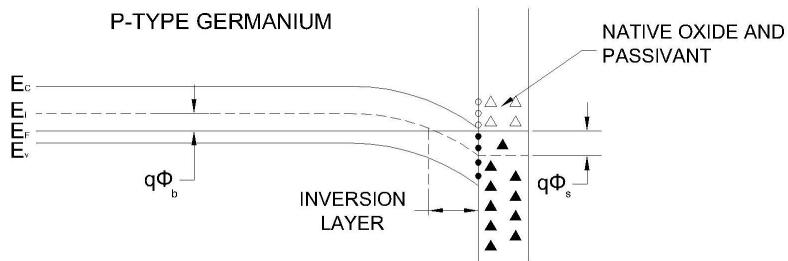


Figure 2. Simplified energy diagram depicting an inversion layer on the surface of P-type HPGe including slow states (▲ neutral, △ positive) and fast states (● neutral, ○ positive). The vertical axis is relative energy (eV), the horizontal axis is displacement (arbitrary units), E_c is the bottom of the conduction band, E_v is the top of the valence band, E_F is the material Fermi level, E_i is the approximate intrinsic Fermi level, Φ_b represents bulk potential, Φ_s represents surface potential, and q is the electron charge. After Brown (1953) and Dinger (1975).

Two large-volume (~100% relative) SEGe detectors will be manufactured using the SiO_x passivant as described in the previous paragraphs. First, baseline data will be established by characterizing each detector using CANBERRA standard test procedures which include the measurement of relative efficiency, electronic noise analysis, resolution measurements, and peak shape measurements. Second, we will measure the reverse leakage current of each detector versus several operating temperatures using a mechanically cooled cryostat. In addition the electronic noise of both detector assemblies will be measured at each operating temperature. These tests should sufficiently characterize the temperature stability of the intercontact surface. The surface characteristics of high-purity germanium can be influenced both by the net impurity concentration at the intercontact surface and by local crystallography. To ensure that the results of the experiments are related to the passivants being tested rather than the characteristics of the specific germanium material, the same detector elements will be used throughout our development efforts.

To test our current passivation method for ruggedness, we will perform three basic tests. First, we intend to remove each device from its vacuum cryostat to perform 10 rapid thermal cycles from 87 K to approximately 300 K. We will then perform careful visual inspections of the devices to determine if cracking or flaking of the passivant is evident. Second, before the test devices are re-installed into their vacuum cryostats, we intend to “age” them at room temperature and atmospheric pressure for one month. We will re-install the devices into their respective vacuum cryostats then perform reverse leakage current and noise tests to determine if the devices survived. Third, we intend to perform three successive overnight vacuum pumping procedures at elevated temperatures (70 C to 100 C), then we will repeat leakage current and noise tests.

The first new surface passivation to be evaluated will be a native oxide film grown on the detector interelectrode surface using a wet chemical oxidation (WCO) technique. Unlike the naturally occurring native germanium oxide which forms on clean germanium from exposure to atmospheric moisture and oxygen or the thick highly non-stoichiometric residual oxide left after most nitric-acid-based etches, oxide films produced by WCO techniques are very dense, homogenous and for the most part defect free. Germanium WCO techniques have been investigated by Gregory et al. (1988) who were successful in growing native GeO_2 with excellent stoichiometry. Gregory also found that the best films remained stable after samples were stored for one year at room temperature. Such films should behave as good passivants for detector interelectrode surfaces primarily because they contain a low density of electronic states which are a direct cause of surface channel formation. Furthermore, if WCO films are dense and continuous as suggested by Rutherford backscattering measurements and electron micrographs, they contain few interstices for the permeation of reactive gas species. By definition a native oxide is grown directly from the germanium surface with a resulting decrease in the density of unconsumed germanium bonds (dangling bonds) which act as charge generation sites. Limiting generation sites may reduce surface leakage temperature sensitivity and reduce surface noise.

Gregory found that using hydrofluoric acid with a trace of hydrogen peroxide creates a water insoluble phase of GeO_2 presumably by preventing the water / hydrofluoric acid soluble phase from accumulating on the germanium surface. For this research, native germanium oxide passivating films will be created using a similar WCO technique which will incorporate a hydrofluoric acid / oxidizer solution. Since a minuscule amount of oxidizer is used in all

WCO techniques (Gregory used less than 1% by volume H₂O₂ for his most successful attempts.), it is imperative to use a stable oxidizer, especially within a commercial laboratory environment. Hydrogen peroxide is generally very stable, however; it can be quickly decomposed by traces of transition metals unless artificially stabilized by the addition of compounds such as stannate salts. To avoid any variability in the growth of native germanium oxide due to unknown concentrations of hydrogen peroxide or the effects of stabilizing agents, we will attempt to substitute a more tolerant oxidizer. Several oxidation experiments will be needed to determine the acceptable oxidizer and ratio of the solution constituents, as well as reaction time and temperature. When we have grown acceptable oxides on the intercontact surfaces of both SEGe devices, we will remount the detectors into their electrically-cooled cryostats. The detectors will be evaluated in the same manner as for the standard SiO_x passivation. Any additional tests required to demonstrate the ruggedness and stability of the oxide passivant will be performed as well. A subsequent progress report will include a summary of the successful film growth technique and test results.

Pioneering work done on the use of sputtered films for HPGe passivants was done by Hansen et al. (1980, 1986). Hansen stated that as passivants for HPGe detector surfaces, sputtered hydrogenated amorphous germanium (α -Ge:H) films demonstrate none of the drawbacks of films produced by silicon monoxide evaporation. Cathodic sputtering of germanium can be accomplished either by DC or AC techniques with AC techniques being more easily controlled especially at low power (~150 W). An argon / hydrogen atmosphere is used to create amorphous germanium films on crystalline germanium surfaces. Because of the innate random stoichiometry of amorphous films, the resulting unsatisfied germanium bonds in the film must be passivated with hydrogen. Also, the impact of ions and neutral atoms alike can break germanium bonds at the crystalline surface which require hydrogen passivation. Ions and neutrals impacting the device surface liberate oxides and other species resulting in a nearly clean surface albeit a damaged one. In addition to α -Ge:H, hydrogenated amorphous silicon (α -Si:H) is another consideration for creating passivant films. More stoichiometric oxide films other than those produced by silicon monoxide evaporation may be formed by adding oxygen rich chemical species such as boron trioxide (B₂O₃) to SiO to formulate a pure borosilicate glass which can subsequently be sputtered to deposit a passivating coating on germanium. Such a film may tolerate pump and bake temperatures exceeding 60 C which are needed to reduce the adsorbed gas load of detector / cryostat assemblies. Also, a more stable film with fewer electronic states than those created by evaporation techniques should produce less pronounced surface effects. Sputtering silicon-based glass requires more power than sputtering germanium which may damage the intercontact surface of a detector to a larger degree than a low-power germanium deposition. As done with sputtered germanium films, an argon / hydrogen atmosphere will be necessary to passivate damage sites. In turn, α -Ge:H, α -Si:H, and borosilicate films will be deposited on the intercontact surfaces of both test SEGe detectors for a total of six depositions. Each test passivant will be tested in the same manner as for the standard SiO_x passivation. Again, additional testing may be required to demonstrate the ruggedness and stability of the passivant. A subsequent progress report will include a summary of the successful film deposition techniques and test results.

RESEARCH ACCOMPLISHED

The contract period for this research began in the second week of June 2008. At the time of this writing no significant research has been accomplished.

CONCLUSIONS AND RECOMMENDATIONS

Our research entails the characterization of several different films used as chemical passivants for the intercontact surface of HPGe photon detectors. We intend to compare the properties of grown native oxide films and sputter deposited films to the properties of a control technique comprising evaporated silicon monoxide films. Successful films must tolerate temperature cycling between room temperature and cryogenic temperatures, they must tolerate being exposed to room temperature at atmospheric pressure for long periods of time, and they must survive vacuum pump and bake cycles at temperatures exceeding 60°C. Passivants must not contain an appreciable density of electronic states which can result in high surface leakage current or high surface noise; therefore, test detectors will be evaluated using standard procedures to determine surface leakage current and noise.

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